Dissipation Dynamic of Insecticide Chlorantraniliprole in Pear Fruits

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Abstract

This study was conducted in order to evaluate the dissipation dynamic of insecticide chlorantraniliprole in pear fruits. Plant protection product (PPP) based on chlorantraniliprole was applied at the recommended rate, for the control of the main pear pest, *Cacopsylla pyri*. For the analysis of insecticide residues, the QuEChERS-based method, followed by HPLC analysis was validated in accordance with SANTE/12682/2019. In this study, the maximum level of the residues in the pear fruits (4.95 mg/kg) was obtained 1h after the application of PPP, i.e., after drying the deposit. After 14 days, the level of chlorantraniliprole was 0.16 mg/kg, which is significantly below the MRL of 0.5 mg/kg. The results indicated that chlorantraniliprole exhibited first-order kinetics dissipation, with a half-life of 2.76 days.

Keywords

Pear, chlorantraniliprole, dissipation dynamic, half-life

1. Introduction

Chlorantraniliprole [3-bromo-N-[4-chloro-2-methyl-6-[(methyl amino) carbonyl] phenyl]-1-(3-chloro-2-pyridinyl)-1H-pyrazole-5-caroxamide] is an anthranilic diamide insecticide. This substance acts on insect ryanodine receptors, playing a critical role in muscle function. Due to its specific structure, it shows remarkable selectivity and safety for mammals [1]. Insecticides based on chlorantraniliprole are used for the control of the most important apple, peach, pear, grape, cabbage, tomato, and potato pests.

The dissipation rate of a pesticide after the application is a useful tool for the assessment of the behavior of its residues. These data are also important for the estimation of pre-harvest interval (PHI), i.e., the time required to reduce the residue levels below the maximum residue limit (MRL) [2, 3]. While a number of studies focus on the efficacy and residues of chlorantraniliprole, there is a lack of research about its behavior in pear fruits [2].

This study was carried out with the aim to evaluate the behavior and the dissipation dynamics of insecticide chlorantraniliprole in pear fruits, after its application at the recommended rate and calculating its half-life. For the determination of chlorantraniliprole residues in pear fruits, the QuEChERS-based method followed by high-performance liquid chromatography (HPLC) has been validated.

2. Material and Methods

2.1. Field Trial

The field trial was carried out at the locality Kula (Republic of Serbia), in 2021. The experiment was conducted according to the standard EPPO methods. Plant protection product based on

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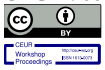

chlorantraniliprole (45 g a. i./l, SC) was foliar applied at the concentration of 0.1%, with water consumption of 1000 l/ha. The treatment was conducted in order to control the presence of *Cacopsylla pyri* in the pear fruits (BBCH 74). The experiment was set up in four replications, as a randomized block system.

To investigate the dissipation dynamics and terminal residue of insecticides, pear fruits were randomly collected at 0 (1 h), 2, 4, 6, 8, 10, 12, and 14 d after the application of chlorantraniliprole, according to the FAO/WHO recommendations [4]. Fresh samples (approx. 500 g) were transferred to the laboratory within 2 h after collection, homogenized and stored at −20 °C before analysis.

2.2. Extraction and Analysis of Insecticide Residues

The content of insecticide residues in the analyzed pear samples was assayed following a QuEChERS procedure [5]. The procedure involved the extraction of 10 g pear fruits with 10 ml acetonitrile. Subsequently, a liquid-liquid partition was performed by adding a mixture of $MgSO_4$, NaCl, trisodium citrate dihydrate, and disodium hydrogen citrate sesquihydrate. After vortex and centrifugation, 6 ml of the aliquot was added into a tube containing 150 mg primary secondary amine (PSA) sorbent and 0.9 g anhydrous $MgSO_4$, as a cleanup step. After the shaking and centrifugation, the extract was evaporated till dry and dissolved in 1 ml of acetonitrile and analyzed.

Detection and quantification were performed with an Agilent 1100 HPLC system (USA), equipped with a photodiode array detector. In terms of chromatographic conditions, a column Zorbax XDE (50 mm × 4.6 mm, 5 μm film thickness) was used. The method was validated through linearity, precision, the limit of detection and quantification (LOD, LOQ), matrix effect, and accuracy.

3. Results and Discussion

The results obtained for the validation parameters are shown in Table 1. The analytical methods have been validated according to SANTE/12682/2019 standard [6].

Table 1
Validation parameters

Insecticide	Linearity	Precision (%)	Recovery (%)	ME (%)	LOD (mg/kg)	LOQ (mg/kg)
Chlorantraniliprole	0.992	0.87	83.4 – 95.9%	104.2	0.05	0.16

Table 2
Dissipation dynamic of chlorantraniliprole in pear fruits

Days after the application	Residues	Persistence (%)	Loss (%)
0*	4.95	100.00	0.00
2	3.29	66.46	33.54
4	2.16	43.64	56.36
6	1.09	22.02	77.98
8	0.51	10.30	89.70
10	0.32	6.46	93.54
12	0.22	4.44	95.56
14	0.16	3.03	96.97

After the application of chlorantraniliprole-based insecticide, the maximum level of the residues in the pear fruits (4.95 mg/kg) was obtained after 1 h, i.e. after drying the deposit (Table 2). In the samples collected two days after the treatment, the average value of chlorantraniliprole residues was 3.29 mg/kg, with a loss of 33.54%.

In the next days, chlorantraniliprole content in pear fruits decreased, and at the end of the pre-harvest interval, it was 0.16 mg/kg. In this study, chlorantraniliprole residues were at the MRL level of 0.5 mg/kg eight days after the application. The dissipation rate of chlorantraniliprole in pear fruits followed the first-order kinetic equation (1) was used [7]:

$$C_t = C_0 \times \exp^{(-k \times t)} \quad (1)$$

where *Ct* is the residual pesticide concentration (mg/kg) at time *t* (days) after application; C_0 is the initial pesticide concentration, and *k* is the pesticide dissipation rate constant. The half-life ($t_{1/2}$) was calculated from the equation:

$$t_{1/2} = \ln(2)/k \quad (2)$$

Table 3
Half-life of chlorantraniliprole in pear fruits

Insecticide	Regression equation	Constant	R^2	DT_{50} (day)
Chlorantraniliprole	$y = 4.95e^{-0.25x}$	0.25	0.988	2.76

In order to describe the dissipation rate of pesticide's active ingredient in crops, first-order kinetics has been extensively used. In this study, the results showed a gradual decrease of chlorantraniliprole in pear fruits, with a correlation coefficient of 0.988 (Table 3). The half-life of chlorantraniliprole in pear fruits, based on the obtained results, was 0.6 days.

According to the available literature, a number of studies dealt with the behavior of chlorantraniliprole in plants [8, 9]. The half-life of chlorantrilantriliprole in cauliflower was 1.36 days [10], while in grapes was 2.70 days [2]. In our previous research, the dissipation dynamic of chlorantraniliprole in peach fruits showed a $t_{1/2}$ of 3.15 days [3]. However, this the first study conducted in peach fruits.

4. Conclusions

In this study, a simple and reliable method for the determination of residues of insecticide chlorantraniliprole in pear fruit was validated. Furthermore, the dissipation dynamic was also studied. The obtained results indicated that chlorantraniliprole degrades rapidly in pear fruits. After the application of chlorantraniliprole-based insecticide for the control of the main pear pest, the half-life was 2.76 days. Obtained results could be useful for the safe use of chlorantraniliprole insecticide in pest management of pear.

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